

NON-DESTRUCTIVE METHOD FOR DETERMINING THE EXTENT OF CURE OF A POLYMERIZING MATERIAL AND THE SOLIDIFICATION OF A THERMOPLASTIC POLYMER BASED ON WAVELENGTH SHIFT OF FLUORESCENCE

FIELD OF THE INVENTION

The present invention relates to a non-destructive method for measuring the extent of cure of a polymerizing material or the extent of solidification of a thermoplastic polymer being processed by injection molding, and, more particularly, to a method which utilizes peak fluorescence wavelength to measure the extent of cure or solidification, and to a class of fluorophores for use in connection therewith.

BACKGROUND OF THE INVENTION

In the manufacture of a variety of products, such as polymer matrix composites and vinyl polymers, as well as in the applications of dental or medical resins, the cure or polymerization reactions of polymerizing materials must be adequately monitored and controlled to produce the desired resultant products. Fluorescence techniques are particularly useful for cure monitoring because they are sensitive and adaptable to non-destructive, in-line, real-time monitoring.

One known fluorescence technique for monitoring the cure of an epoxy resin is disclosed in Wang, et al., 27 *Polymer* 1529 (1986), which is herein incorporated by reference. According to the technique, a trace amount of 1-(4-dimethylaminophenyl)-6-phenyl-1,3,5-hexatriene ("DMA-DPH"), which is a viscosity-sensitive fluorophore, and a trace amount of 9,10-diphenylanthracene ("DPA"), an internal standard fluorophore which is insensitive to viscosity, are dissolved in an epoxy resin. The fluorescence intensities of the viscosity-sensitive fluorophore, DMA-DPH, and the internal standard, DPA, are then measured at various cure times. Finally, the ratio of these intensities, which is insensitive to the change in the shape of the sample or the presence of filler particles, is used to monitor the cure of the epoxy resin. An advantage of this technique is that the use of two fluorophores eliminates inaccuracies in measuring the absolute fluorescence intensity of a viscosity-sensitive fluorophore when the polymerizing material contains filler particles or undergoes polymerization shrinkage. However, the method suffers from the drawback that the two fluorophores may have overlapping fluorescence spectra, thereby necessitating complicated deconvolution of the fluorescence spectra.

U.S. Pat. No. 4,651,011 to Ors and Scarlata, also incorporated herein by reference, discloses another method of determining the extent of cure of a polymerizing material in which the change in fluorescence anisotropy of a fluorophore dissolved in a polymerizing material is measured. In contrast to the above-described method of Wang, et al., the method of Ors and Scarlata utilizes only one fluorophore. However, a major drawback of the method is that it requires the use of a complex optical system. In particular, the method uses polarized exciting radiation, together with polarizers for separating fluorescence intensities in two mutually perpendicular directions.

SUMMARY OF THE INVENTION

Thus, it is a purpose of the present invention to overcome the disadvantages of the prior art and thereby provide a relatively simple method of determining the extent of cure of

a polymerizing material or the extent of solidification of a thermoplastic polymer and to provide a class of fluorophores for use in the method.

According to the method of the invention, the extent of cure of a polymerizing material or the extent of solidification of a thermoplastic polymer are measured by first dissolving a fluorophore in the polymerizing material or thermoplastic polymer. The change in peak fluorescence wavelength of the fluorophore is then measured and compared with a known value to determine extent of cure or extent of solidification.

The fluorophores of the invention undergo a large change in the electronic charge distribution upon absorption of light, and include compounds comprising substituted linear alkenes having an electron accepting group and an electron donating group. Preferably, the electron accepting group is attached at the alpha position and the electron donating group is attached at the omega position of the linear alkene. The electron accepting group is selected from the group consisting of 4-pyridinium alkylsulfonate, para-substituted phenyl, 1-naphthyl substituted at the 5-position, and 2-naphthyl substituted at the 6-position. The substituent of the para-substituted phenyl, 1-naphthyl and 2-naphthyl groups is selected from the group consisting of nitro, sulfoamido, sulfonate, cyano, acyl and carboxylic ester groups. The electron donating group is selected from the group consisting of 4-(N,N-dialkylanilino), 6-[2-(N,N-dialkylamino)naphthyl] and 1-[5-(N,N dialkylamino)naphthyl].

It is, therefore, an object of the present invention to provide a method of monitoring the extent of cure of a polymerizing material or the extent of solidification of a thermoplastic polymer by measuring change in peak fluorescence wavelength of a fluorophore.

It is another object of the present invention to provide a class of fluorophores which exhibit a relatively large change in peak fluorescence wavelength for use in the method of the invention.

It is another object of the invention to provide a class of fluorophores which absorb light in the visible range.

It is still another object of the invention to provide a device for use in connection with measuring change in peak fluorescence wavelength during the curing of a polymerizing material or the solidification of a thermoplastic polymer.

These and other objects of the present invention will become apparent from the detailed description to follow.

BRIEF DESCRIPTION OF THE DRAWINGS

There follows a detailed description of the preferred embodiments of the present invention which are to be taken together with the accompanying drawings, wherein:

FIG. 1 shows a graph of peak fluorescence wavelength and fluorescence intensity versus cure time during the cure of DMA-DPH in a stoichiometric mixture of diglycidyl ether of bisphenol A ("DGEBA") and diethylene triamine ("DETA") at 50° C.

FIG. 2 shows a diagram of an optical fiber probe for use in conjunction with the method of the invention.

FIG. 3 shows a diagram of another optical fiber probe for use in conjunction with the method of the invention which utilizes evanescent waves to produce fluorescence emission.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the method of the invention, a trace amount of a fluorophore, i.e., typically 10 to 100 ppm by weight, is